Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information for

1,2-Diarylbenzene as Fast T-type Photochromic Switch

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Table S1. Calculated activation energy (E_a) for the thermal cycloreversion and energy gap (ΔE) between the open- and closed-ring isomers.

	Energy (open-ring isomer) /hartree	Energy (closed-ring isomer) /hartree	Energy (transition state) /hartree	E_a /kJ mol^{-1}[a]	ΔE /kJ mol^{-1}[b]
1	−2434.737169	−2434.715696	−2434.666894	128.15	56.39
2	−2273.147373	−2273.105085	−2273.083204	57.46	111.04

[a] E_a = Energy(transition state) − Energy(closed-ring isomer). [b] ΔE = Energy(closed-ring isomer) − Energy(open-ring isomer).

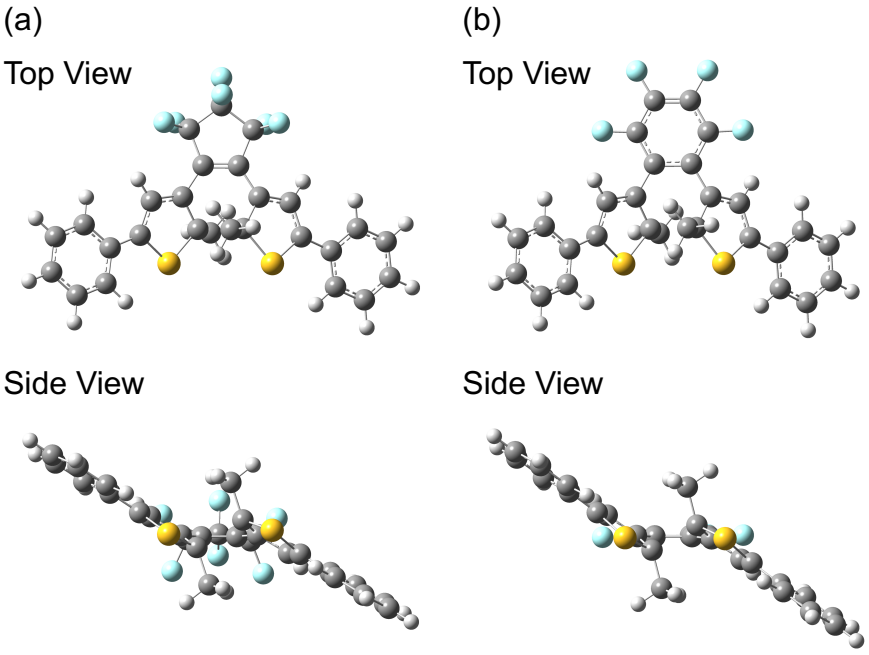

Fig. S1. Molecular structures of (a) **1** and (b) **2** in the transition state optimized at the B3LYP/6-31G(d) level.

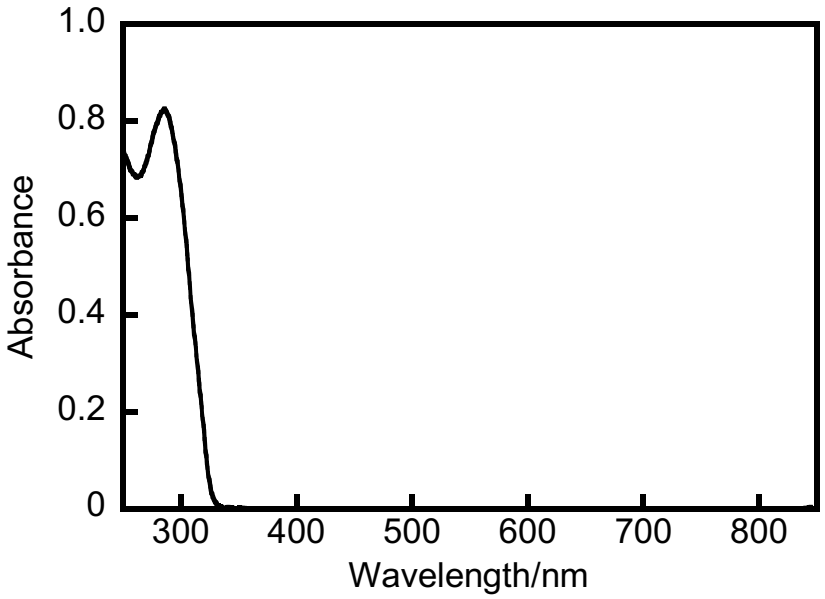

Fig. S2 Absorption spectrum of **2a** in *n*-hexane at 298 K ([**2a**] = 2.7 × 10^{-5} M).

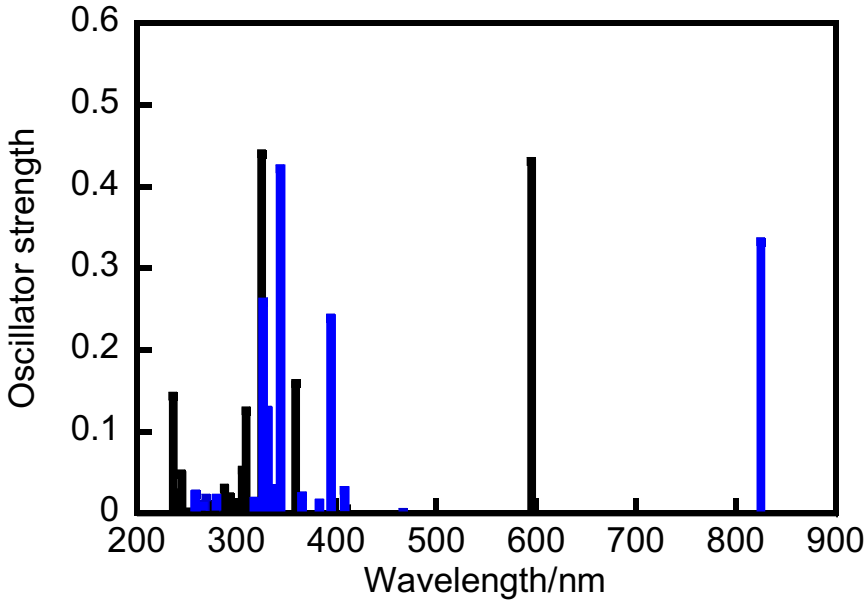

Fig. S3. Oscillator strength of **1b** (black line) and **2b** (blue line) calculated by time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) level.

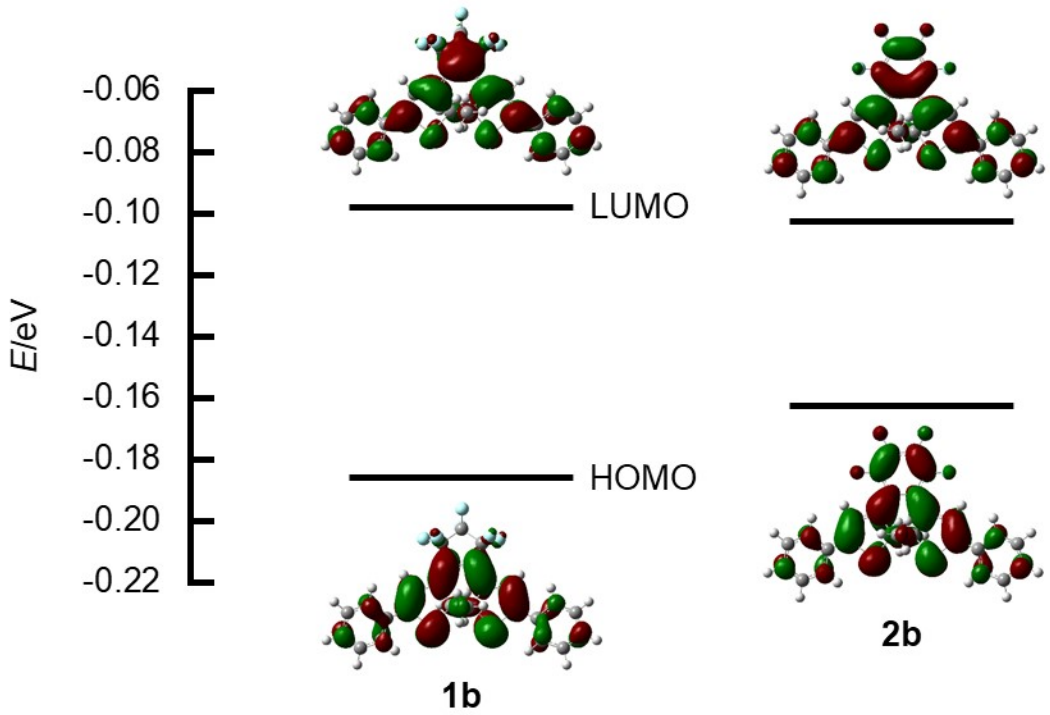

Fig. S4. Molecular orbitals and energies of **1b** and **2b** calculated by density functional theory (DFT) at the B3LYP/6-31G(d) level.

Table S2. HOMO and LUMO level data of **1b** and **2b** calculated by density functional theory (DFT) at the B3LYP/6-31G(d) level.

	E_{LUMO}/eV	E_{HOMO}/eV	$\Delta E_{HOMO\text{-}LUMO\ gap}$/eV
1b	−0.09753	−0.18541	−0.08788
2b	−0.10185	−0.16258	−0.06073

Kinetic analysis of thermal cycloreversion reaction

The reaction kinetics of the thermal cycloreversion was analyzed as follows: If the thermal cycloreversion reaction from the closed-ring isomer to the open-ring isomer obey a first-order kinetics, the kinetic equation is expressed as following equation by using Lambert-Beer law.

$$\ln\frac{A_t}{A_0} = -kt$$

where k is reaction rate constant, t is reaction time, and A_0 and A_t are absorbance of the closed-ring isomer at initial state (t = 0 s) and at arbitrary reaction time t, respectively. The k value can be calculated from the slope of the linear plot as shown in Fig. S5. The calculated k values are summarized in Table S3.

Arrhenius equation can be described as follows.

$$\ln k = \ln A - \frac{E_a}{RT}$$

where A is frequency factor, E_a is activation energy, R is gas constant, and T is absolute temperature. The linear relationship can be obtained by plotting ln$k$ relative to 1/T as shown in Figure 4b. The E_a and A values can be determined from the slope and intercept of the linear plot. The results are summarized in Table 1.

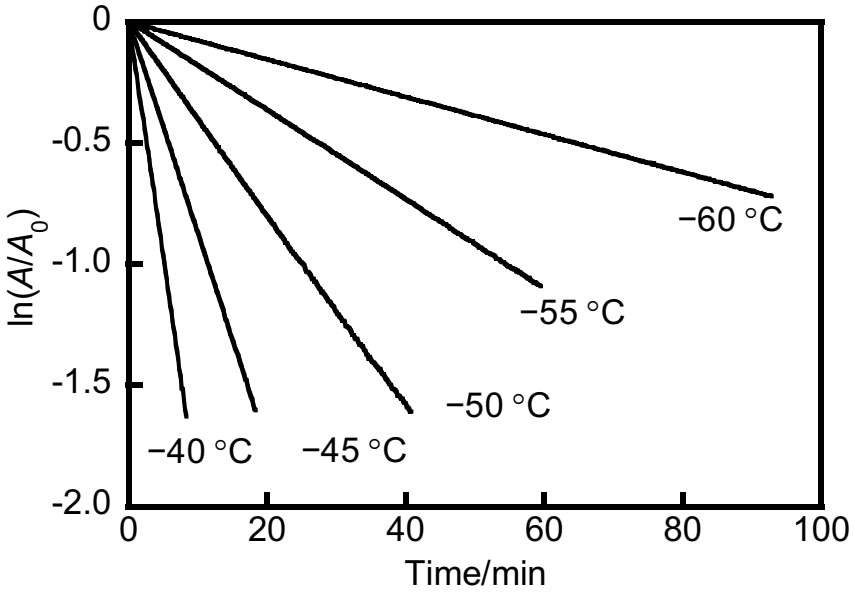

Fig. S5. First-order kinetic profiles of **2b** monitored at 745 nm in *n*-hexane.

Table S3. First-order rate constants for the thermal cycloreversion reaction of **2b**.

T/K	k/s^{-1}
233.15	0.003232
228.15	0.001453
223.15	0.000663
218.15	0.000305
213.15	0.000129

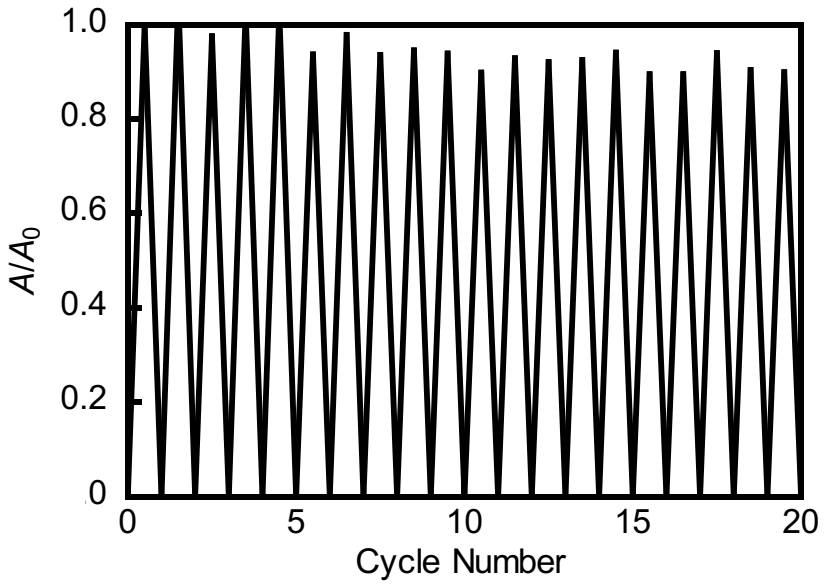

Fig. S6. Absorbance changes of **2b** in *n*-hexane upon cycles of alternating photoirradiation at 313 nm (0.63 mW cm^{-2}) for 150 s at 193 K and thermal bleaching at room temperature.

Table S4. X-ray crystallographic data for **2a**.

Formula	$C_{28}H_{18}F_4S_2$
Formula weight	494.54
Temperature/K	150(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a/Å	7.5411(3)
b/Å	14.0447(5)
c/Å	22.0416(9)
α/deg	90
β/deg	90
γ/deg	90
Volume/Å^3	2334.48(16)
Z	4
Density/g cm^{-3}	1.407
Goodness-of-fit on F^2	1.066
R ($I > 2\sigma(I)$)	R_1 = 0.0372
R (all data)	$wR2$ = 0.0909
CCDC No.	1872163

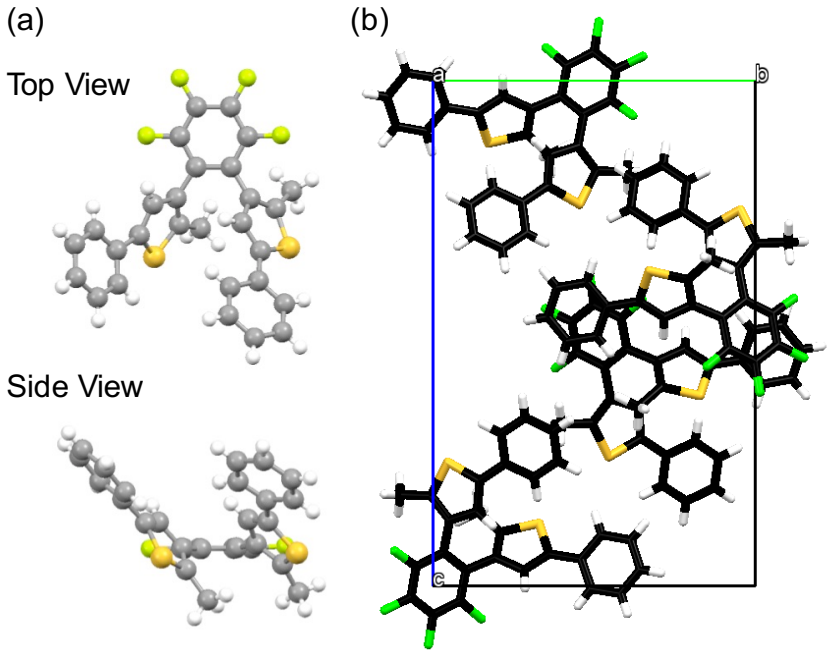

Fig. S7. (a) Molecular structure and (b) packing diagram of **2a** in crystal.

Table S5. Cartesian coordinates of **1a** optimized at the B3LYP/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	1.254262	2.651505	0.128012
C	0.032710	3.598297	0.178398
C	-1.128258	2.722625	-0.352850
C	-0.655137	1.295236	-0.180249
C	0.662670	1.260078	0.149634
C	-1.572605	0.187332	-0.482312
C	1.535094	0.128860	0.479953
C	-2.901540	0.095276	0.054819
H	-3.313368	0.836005	0.727993
C	-3.610324	-0.994231	-0.380191
C	-1.281498	-0.837749	-1.364937
C	1.210574	-0.908203	1.335776
C	2.875513	0.031020	-0.027366
H	3.289290	0.753261	-0.720794
C	3.562252	-1.072950	0.404311
S	-2.632623	-1.926471	-1.501057
S	2.551628	-2.006276	1.495460
C	4.932066	-1.488406	0.076317
C	7.564759	-2.253636	-0.576705
C	5.323713	-2.837973	0.122578

C	5.890258	-0.528550	-0.299033
C	7.188541	-0.909420	-0.628189
C	6.626849	-3.214703	-0.196027
H	4.597162	-3.599943	0.392477
H	5.617903	0.522626	-0.311035
H	7.912715	-0.151126	-0.913654
H	6.906479	-4.263962	-0.154678
H	8.579963	-2.548084	-0.827609
C	-4.974164	-1.403220	-0.020141
C	-7.597704	-2.149840	0.690774
C	-5.523153	-1.021155	1.217847
C	-5.766688	-2.172279	-0.890533
C	-7.061787	-2.544463	-0.536201
C	-6.822013	-1.384433	1.564395
H	-4.918849	-0.451018	1.917238
H	-5.372771	-2.463412	-1.860713
H	-7.656578	-3.136670	-1.226377
H	-7.225403	-1.078175	2.525886
H	-8.608739	-2.437684	0.965036
C	-0.046916	-1.146552	2.116344
H	-0.546712	-0.197413	2.331064
H	0.165487	-1.641831	3.069343

H	-0.757928	-1.772336	1.563133
C	-0.044602	-1.073416	-2.179330
H	0.465566	-0.126305	-2.377759
H	-0.285463	-1.536857	-3.141408
H	0.667758	-1.726703	-1.660589
F	1.951907	2.869672	-1.035103
F	2.110120	2.888515	1.152698
F	-0.210076	3.936697	1.468947
F	0.209893	4.722627	-0.543118
F	-2.280961	2.990128	0.327403
F	-1.365088	3.011169	-1.663999

Table S6. Cartesian coordinates of **1b** optimized at the B3LYP/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-1.222696	2.986518	0.172954
C	-0.010871	3.836799	-0.304748
C	1.236428	2.986858	0.077776
C	0.721715	1.578639	0.108326
C	-0.723892	1.578231	0.061674
C	1.435073	0.420581	0.207718
C	-1.436292	0.426382	-0.092509
C	-2.845727	0.207721	-0.099515
H	-3.551127	1.029516	-0.124156
C	-3.226550	-1.105040	-0.058415
C	-0.641497	-0.857352	-0.389055
C	2.842355	0.201803	0.158029
H	3.550163	1.022366	0.158076
C	3.221548	-1.110341	0.082048
C	0.642184	-0.870191	0.475641
S	1.844350	-2.238573	0.049113
S	-1.848294	-2.233005	0.000384
C	-0.363443	-0.898044	-1.913754
H	0.282104	-0.064781	-2.207952
H	-1.309428	-0.810737	-2.453900

H	0.120537	-1.833046	-2.202480
C	0.366241	-0.947922	1.998877
H	-0.278546	-0.121810	2.314032
H	1.313064	-0.873998	2.539689
H	-0.117526	-1.889625	2.265741
C	-4.597441	-1.624279	-0.038458
C	-7.241935	-2.597346	-0.014616
C	-5.670349	-0.793897	0.344181
C	-4.880845	-2.955471	-0.397067
C	-6.189087	-3.434128	-0.386905
C	-6.975136	-1.275168	0.352264
H	-5.475555	0.227291	0.656100
H	-4.072647	-3.611655	-0.705991
H	-6.385172	-4.463465	-0.673999
H	-7.786632	-0.618671	0.653863
H	-8.261689	-2.971883	-0.004807
C	4.591095	-1.627775	0.004572
C	7.232899	-2.598474	-0.131290
C	5.647574	-0.793259	-0.412986
C	4.888952	-2.961649	0.340907
C	6.195994	-3.439154	0.275473
C	6.951214	-1.273582	-0.476573

H	5.440266	0.230106	-0.709337
H	4.093845	-3.620837	0.676377
H	6.403722	-4.470568	0.546439
H	7.749851	-0.614103	-0.804787
H	8.251669	-2.972051	-0.184260
F	-2.337053	3.245400	-0.565751
F	-1.510556	3.334592	1.467035
F	-0.068093	3.949064	-1.657093
F	0.011286	5.069929	0.235972
F	1.691227	3.397620	1.301870
F	2.258874	3.182334	-0.804020

Table S7. Cartesian coordinates of transition state of **1** optimized at the B3LYP/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.636455	1.598124	0.261004
C	1.383495	0.38193	0.536034
C	0.647573	-0.851103	0.808247
C	-0.633762	-0.853075	-0.813733
C	-1.371705	0.37513	-0.534238
C	-0.63832	1.590499	-0.238371
S	-1.831082	-2.192572	-0.789631
C	-3.175774	-1.13065	-0.361906
C	-2.736457	0.190249	-0.292757
C	2.748623	0.198113	0.295765
C	3.188338	-1.123764	0.356687
S	1.84491	-2.189105	0.776588
C	4.522061	-1.63712	0.085091
C	-0.304787	-0.944226	1.990196
C	0.318653	-0.939824	-1.995964
C	-1.195952	2.97731	-0.338022
C	4.761501	-3.016434	-0.092266
C	6.042144	-3.49454	-0.351781
C	0.044929	3.901104	-0.173378
C	6.903609	-1.243262	-0.263782

C	1.122148	2.997116	0.494627
C	5.626332	-0.7602	-0.003379
F	-0.223785	5.001283	0.55762
F	0.476506	4.284509	-1.399692
F	2.355976	3.235626	-0.046458
F	1.217034	3.290241	1.82392
F	-1.835786	3.214814	-1.513493
F	-2.103496	3.233902	0.659996
H	-1.028723	-0.126853	1.974051
H	-0.854395	-1.890516	1.980551
H	0.256392	-0.883025	2.928783
H	1.044657	-0.124408	-1.973187
H	0.866254	-1.887287	-1.992767
H	-0.241863	-0.870761	-2.934421
H	3.933313	-3.71769	-0.039227
H	6.197023	-4.561438	-0.487929
H	7.735738	-0.547011	-0.324013
H	5.482534	0.304857	0.148786
C	7.121588	-2.612813	-0.44082
H	8.120994	-2.98741	-0.642776
C	-4.509146	-1.646859	-0.09343
C	-4.747273	-3.027002	0.078278

C	-5.614167	-0.771219	-0.00306
C	-6.027845	-3.507273	0.334286
H	-3.918281	-3.727162	0.023464
C	-6.891308	-1.256401	0.254105
H	-5.471082	0.294478	-0.151557
C	-7.10815	-2.62684	0.425482
H	-6.181974	-4.574835	0.46595
H	-7.724171	-0.561183	0.315952
H	-8.107481	-3.003159	0.624591
H	3.396567	1.017373	0.009012
H	-3.381608	1.00767	0.008905

Table S8. Cartesian coordinates of **2a** optimized at the B3LYP/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.651362	4.158176	0.241900
C	-0.660541	1.711563	-0.259521
C	-0.651393	4.158180	-0.241846
C	1.285522	2.944040	0.484417
C	0.660523	1.711558	0.259478
C	-1.285547	2.944051	-0.484414
C	1.420620	0.476238	0.590709
C	-1.420634	0.476250	-0.590780
C	-2.678364	0.158942	0.020062
H	-3.149464	0.802307	0.754767
C	2.678349	0.158934	-0.020119
H	3.149450	0.802291	-0.754831
C	3.250791	-1.003316	0.430265
C	1.044302	-0.446691	1.542930
C	-1.044326	-0.446670	-1.543003
C	-3.250783	-1.003328	-0.430291
S	-2.222183	-1.727306	-1.654300
S	2.222189	-1.727283	1.654281
C	-4.513540	-1.626327	-0.013816
C	-6.946225	-2.792683	0.809128

C	-5.234640	-2.475767	-0.871902
C	-5.036758	-1.379263	1.269155
C	-6.241737	-1.949601	1.671449
C	-6.433856	-3.055043	-0.462548
H	-4.861975	-2.668874	-1.874319
H	-4.482874	-0.750199	1.959867
H	-6.625526	-1.744172	2.667280
H	-6.973735	-3.706667	-1.144376
H	-7.882931	-3.242455	1.126313
C	4.513565	-1.626305	0.013832
C	6.946279	-2.792650	-0.809048
C	5.036821	-1.379235	-1.269123
C	5.234645	-2.475742	0.871937
C	6.433875	-3.055013	0.462612
C	6.241812	-1.949567	-1.671387
H	4.482955	-0.750170	-1.959850
H	4.861958	-2.668853	1.874344
H	6.973736	-3.706635	1.144455
H	6.625628	-1.744132	-2.667206
H	7.882994	-3.242420	-1.126208
C	-0.160379	-0.458123	2.435728
H	-0.591158	0.545214	2.500363

H	0.099120	-0.779759	3.450265
H	-0.941116	-1.129981	2.059513
C	0.160321	-0.458084	-2.435852
H	0.941160	-1.129784	-2.059564
H	0.590975	0.545295	-2.500664
H	-0.099179	-0.779915	-3.450325
F	-1.278777	5.314494	-0.483249
F	-2.537099	2.989701	-0.973468
F	1.278741	5.314481	0.483344
F	2.537079	2.989678	0.973460

Table S9. Cartesian coordinates of **2b** optimized at the B3LYP/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.708926	4.218600	-0.031568
C	-1.398209	3.039378	-0.108884
C	0.738125	1.763809	-0.031848
C	-0.742113	1.762817	-0.009150
C	1.392322	3.044429	0.018025
C	-0.716564	4.215763	-0.108062
C	-1.433946	0.561595	0.132325
C	1.431876	0.559552	-0.123913
C	2.829385	0.303402	-0.080055
H	3.563465	1.095195	-0.079954
C	-2.829122	0.300498	0.077063
H	-3.561268	1.088385	-0.016641
C	-3.191838	-1.024228	0.083813
C	3.193741	-1.019772	-0.035275
C	-0.630925	-0.701034	0.467634
S	-1.796366	-2.121904	0.124444
S	1.798740	-2.117889	-0.002340
C	0.630637	-0.717144	-0.406708
C	4.554462	-1.555231	0.003402
C	7.184404	-2.577690	0.071673

C	5.649287	-0.724150	0.323253
C	4.813595	-2.912777	-0.270902
C	6.112122	-3.415181	-0.238470
C	6.944052	-1.229415	0.353522
H	5.480497	0.319631	0.567691
H	3.992046	-3.573474	-0.531432
H	6.285523	-4.464768	-0.459667
H	7.770047	-0.569846	0.605431
H	8.197023	-2.970264	0.098548
C	-4.550620	-1.561098	0.037487
C	-7.176918	-2.588834	-0.076228
C	-4.787548	-2.921507	-0.242976
C	-5.667185	-0.729819	0.269592
C	-6.960047	-1.237576	0.209715
C	-6.083617	-3.427007	-0.300139
H	-3.949625	-3.587155	-0.429704
H	-5.518509	0.316638	0.515585
H	-7.803185	-0.577806	0.395525
H	-6.238897	-4.479242	-0.522012
H	-8.188077	-2.983740	-0.118878
C	-0.344109	-0.702657	1.993925
H	-1.292797	-0.633651	2.531840

H	0.276936	0.154200	2.271438
H	0.167266	-1.616930	2.301262
C	0.343334	-0.780096	-1.931323
H	-0.278058	0.064478	-2.243645
H	-0.167723	-1.706624	-2.200324
H	1.291834	-0.732180	-2.471978
F	2.739436	3.108831	0.067661
F	1.340101	5.399488	-0.013137
F	-1.350068	5.393879	-0.171058
F	-2.745640	3.100700	-0.154836

Table S10. Cartesian coordinates of transition state of **2** optimized at the B3LYP/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.713385	-0.070552	1.792418
C	0.713385	0.070552	1.792418
C	1.370224	0.124323	3.019784
C	0.68962	0.062972	4.239216
C	-0.68962	-0.062972	4.239216
C	-1.370224	-0.124323	3.019784
C	-1.442795	-0.208941	0.519186
C	-2.491067	-1.107987	0.302489
C	-2.881794	-1.267285	-1.02626
H	-2.927685	-1.690728	1.104348
C	1.442795	0.208941	0.519186
C	2.491067	1.107987	0.302489
C	2.881794	1.267285	-1.02626
H	2.927685	1.690728	1.104348
S	-1.92399	-0.211928	-2.062012
S	1.92399	0.211928	-2.062012
C	-0.912625	0.390834	-0.697668
C	0.912625	-0.390834	-0.697668
C	-0.68962	1.895073	-0.782864
H	-1.65059	2.41544	-0.71781

H	-0.057091	2.24384	0.036148
H	-0.213163	2.172052	-1.728267
C	0.68962	-1.895073	-0.782864
H	1.65059	-2.41544	-0.71781
H	0.057091	-2.24384	0.036148
H	0.213163	-2.172052	-1.728267
F	-2.711952	-0.232738	3.077553
F	-1.365568	-0.120896	5.391941
F	1.365568	0.120896	5.391941
F	2.711952	0.232738	3.077553
C	3.880269	2.178107	-1.56349
C	3.958137	2.460138	-2.944292
C	4.815241	2.807221	-0.710843
C	4.918637	3.333032	-3.445938
H	3.248944	2.000428	-3.627144
C	5.772031	3.679368	-1.21747
H	4.801437	2.594927	0.353664
C	5.831487	3.950187	-2.587778
H	4.95212	3.53426	-4.513371
H	6.480946	4.146569	-0.538999
H	6.581712	4.630411	-2.980784
C	-3.880269	-2.178107	-1.56349

C	-3.958137	-2.460138	-2.944292
C	-4.815241	-2.807221	-0.710843
C	-4.918637	-3.333032	-3.445938
H	-3.248944	-2.000428	-3.627144
C	-5.772031	-3.679368	-1.21747
H	-4.801437	-2.594927	0.353664
C	-5.831487	-3.950187	-2.587778
H	-4.95212	-3.53426	-4.513371
H	-6.480946	-4.146569	-0.538999
H	-6.581712	-4.630411	-2.980784